

POSSIBLE MECHANISM OF FORMATION AND STABILITY OF ANOMALOUS STATES OF WATER

CHEUK-YIN WONG

Oak Ridge National Laboratory, Oak Ridge, TN 37831

SHUI-YIN LO

American Technology Group, Monrovia, CA 91016

California Institute of Technology, Pasadena, CA 91125

We examine the physical processes which are involved in the formation and stability of the anomalous states of water reported recently. The initial step of adding a small amount of ionic compound X^+Y^- to pure water leads to the formation of water clusters $X^+(H_2O)_n$ and $Y^-(H_2O)_n$ with $n \gg 1$. The structure of the cluster around the ion depends strongly on the equation of state. We explore the consequences of possible polymorphic states of H_2O in the liquid phase at room temperature. If there are low-lying polymorphic states, the local dipole moment and the local density will change discontinuously as a function of the radial distance from the ion, and regions of different polymorphic states will be found at different separations from the ion. Fragmentation of the cluster by vigorous shaking may break up the cluster into small domains to allow subsequent coalescence of these domains or the growth of the domains as seeds to form greater domains of polymorphic states. Further experimental and theoretical analyses are needed to study these pictures.

1 Introduction

Recently, experimental observations of anomalous states of water with I_E structures have been reported¹⁻³. The existence of anomalous states of water is an interesting and new phenomenon with important experimental and theoretical implications. It is therefore essential that the observations be confirmed by an independent experimental group in order to ascertain or refute the existence of the anomalous states. While we await such a confirmation, it is useful to make plausible hypotheses on the nature of the anomalous states so as to guide further experimental and theoretical studies on this interesting subject.

The addition of a small amount of ionic compound X^+Y^- to pure water is a necessary step in the production of the I_E water. We shall first consider the formation of clusters brought about by the addition of a small amount of X^+Y^- in water. In such a dilute aqueous solution, the X^+ and Y^- ions are well separated and become isolated. Stable large water clusters of the type $X^+(H_2O)_n$ and $Y^-(H_2O)_n$ will form around the ions in the dilute aqueous solution since similar isolated clusters of $X^+(H_2O)_n$ and $Y^-(H_2O)_n$ are found to

be stable aggregates in many experiments⁴⁻¹³. Specifically, individual assembly of $X^+(H_2O)_n$ and $Y^-(H_2O)_n$, with $X^+=H^+$, Li^+ , Na^+ , K^+ , Ca^{+2} , and $Y^-=Cl^-$, Br^- , I^- , and OH^- have been observed⁴⁻¹³. Similar cooperative effects on complexes of alcohol with proton acceptors have also been observed¹⁴. For the $H^+(H_2O)_n$ cluster, a cluster size up to $n = 75$ has been identified⁷, indicating the stability of large clusters with $n \gg 1$. The limiting size of n has not yet been determined. Computer simulation shows that the six water molecules in the $Na^+(H_2O)_6$ cluster prefer the 4+2 structure, with the Na^+ ion in the center of the shells¹⁵. Molecular dynamics calculations of the hydration shell around an ion in a supercritical aqueous solution also exhibits the clustering of H_2O molecules around an ion¹⁶. One expects, therefore, that in a water solution with a small amount of ionic substance, large H_2O clusters will form around the ions. These large H_2O clusters carry charges and interact among themselves. They may arrange themselves in an orderly manner in the aqueous solution to give rise to clusters of even larger sizes (superclusters) consisting of many $X^+(H_2O)_n$ and $Y^-(H_2O)_n$ clusters. While each $X^+(H_2O)_n$ or $Y^-(H_2O)_n$ may be only about 10 Å in radius, it is interesting to find out whether superclusters may be formed and may be an important component of the I_E water, where clusters of the size of 100-1000 Å have been observed^{1,3}. Thus, the study of these clusters in I_E water will provide information on the stability and the interactions of the $X^+(H_2O)_n$ and $Y^-(H_2O)_n$ in aqueous solutions.

Other interesting physics questions can also be studied with I_E water. The consideration of cluster formation leads to the examination of the structure of the water cluster around an individual ion. One finds that the stability of the cluster arises from the strong Coulombic polarizing power of the ion, which attracts water molecules with their dipole moments aligned along the electric lines of force of the ion. The density and the average local dipole moment of the medium need not be spatially uniform near the ion. Their profiles depend on the equation of state of the water medium as a function of both the density and the average local dipole moment per molecule.

The dependence of the cluster structure on the equation of state leads to another related and interesting subject. It is well known that under different conditions H_2O molecules form different stable structures^{17,18,19} represented by different energy minima around which the many-body state of H_2O can be locally stable. The study of the structure of the cluster around an ion in I_E water will provide vital information on the equation of state of water in the dipole moment and the density degrees of freedom. We shall see that if there are low-lying polymorphic states in water, the dipole moment or density will change abruptly as a function of the radial distance from the ion.

Rigorous motion of the liquid will lead to the fragmentation of the cluster into small domains. The dipole moment of each fragmented domain has been aligned by the ions. If the equation of state of water at room temperature has polymorphic states as exhibited by the presence of multiple minima in densities and dipole moments, then these small domains may coalesce to form larger domains of metastable phases of water¹. The domains may also be the seeds for the growth of larger domains of the same polymorphic states¹. The presence of these metastable polymorphic states of water may be important components of the I_E water. They may then appear as an immiscible mixture without the ions in the aqueous solution. The existence of polymorphic states can be examined by studying whether the medium responsible for the I_E water contains the X^+ and the Y^- ions in the anomalous state. This signature for the existence of polymorphic states can be tested with future experimental investigations.

In the following, we shall review the tetrahedron structure of a H_2O molecule, the structure of a water cluster around an ion, the existence of polymorphic states of H_2O in different phases, and the possibility of multiple energy minima of the states of water with different dipole moments and densities at room temperature.

2 Molecular Structure of H_2O

As is well known, the H_2O molecule has the structure of a tetrahedron. The six electrons of the oxygen atom in the outermost shell and the two electrons from the hydrogen atoms form an octet structure of four ee pairs. The four electron pairs coming out from the oxygen nucleus as the four supports of the tetrahedron, with the two hydrogen nuclei at two vertices of the tetrahedron, are shown in Figure 1. The opening angle between the two O-H bonds is 104.45° as compared to 109.5° for a regular tetrahedron. Thus, the four vertices of the tetrahedron can be characterized as two positively charged H vertices and two negatively charged ee pair vertices.

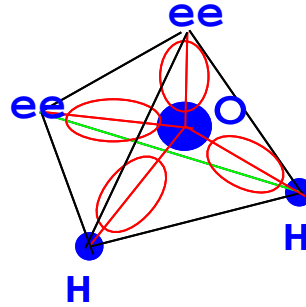


Fig. 1

Because of the complex geometry of the tetrahedron, many possible arrangements of the tetrahedron network lead to stable configurations – the polymorphic states. They differ in their energies. However, under a change of thermodynamical conditions, the lowest-lying polymorphic state may change

to lie higher than another polymorphic state and the role of the ground state changes. The change of thermodynamical conditions will lead to a phase transition between different polymorphic states. Phase transition in which the order parameter changes abruptly is a first-order phase transition. Phase transition in which the order parameter changes continuously is a second-order phase transition.

In the normal liquid state of water, the tetrahedrons of neighboring H_2O molecules are arranged in such a way that the H vertex of one tetrahedron is in the close vicinity of the ee vertex of another tetrahedron, forming a hydrogen bond. A hydrogen bond is weak. It is about 30 times weaker than a normal covalent bond, with a strength of 10-40 kJ/mol²⁰.

For a single H_2O molecule, there is an electric dipole moment with a magnitude of 1.87×10^{-18} esu which is $0.39|e|\text{\AA}$. The electric dipole moment is a vector which points from the oxygen nucleus to the mid-point between the two hydrogen nuclei. For a collection of H_2O molecules, one can also speak of the specific dipole moment which can be defined as the local per-molecule average of the vector sum of the dipole moments of a local collection of H_2O molecules. Because of the vector addition of the dipole moments of individual molecules, the specific dipole moment of a many-body state of H_2O can be quite different if the orientations of the molecules are not random. Different arrangements of the orientation of the molecules will lead to different specific dipole moments. An orderly arrangement of the molecules such that the dipole moments are aligned nearly in the same direction will lead to an increase of the magnitude of the specific dipole moment.

For brevity of notation, we shall use the term “dipole moment” as an abbreviation to refer to the vector or the magnitude of the electric dipole moment, the vector or the magnitude of the electric dipole moment in units of the electron charge, or the vector or the magnitude of the local average of the dipole moment per molecule (the specific dipole moment), as the case may be. The meaning of the different cases can be simply inferred from the context. We shall use the unabbreviated term if its usage will help the understanding of the discussed concepts.

3 The Structure of a H_2O Cluster Around an Ion

Experimental observations⁴⁻¹³ of water clusters of the type $\text{X}^+(\text{H}_2\text{O})_n$ and $\text{Y}^-(\text{H}_2\text{O})_n$ show that the occurrence of water molecules clustering around an ion is a common phenomenon. This arises from the strong Coulombic polarizing power of the ion. For an isolated assembly of large $\text{X}^+(\text{H}_2\text{O})_n$ or $\text{Y}^-(\text{H}_2\text{O})_n$, is the charge located at the center of an isolated cluster or at its

surface? The interaction of the dipole moments of H_2O molecules with the ion depends on the orientation of the dipole moments. The energy of the system is lowest when the dipole moments are aligned along the lines of force of the ionic charge. Then the interaction between a H_2O molecule of dipole moment d with an ion of charge $q|e|$ varies with distance to the ion r as $-|q|e^2d/r^2$, and one can show that the energy is a minimum when the ion is located at the center. Thus, for a large H_2O cluster in equilibrium, the ion is located at the center.

The largest value of n in the $\text{H}^+(\text{H}_2\text{O})_n$ cluster which has been observed⁷ so far is 75. What is the limiting value of n for which the $\text{X}^q(\text{H}_2\text{O})_n$ cluster is still stable? Those H_2O molecules with a binding energy greater than the thermal energy will not be evaporated by thermal motion. Thus, the condition for the H_2O at the outermost H_2O to be bound is

$$\frac{|q|e^2d}{r^2} \geq kT \quad \text{or} \quad r \leq \sqrt{\frac{|q|e^2d}{kT}}. \quad (1)$$

For room temperature with $kT = 0.025$ eV and a water molecule with $d = 0.39|e|\text{\AA}$, the maximum radius of the cluster is $r \sim 15$ \AA , and the maximum number of water molecules n is about 500. If the dipole moments are not completely aligned along the direction of the lines of force of the ion, these values will be reduced. One expects therefore that the radius of the cluster is of the order of 10-15 \AA and a maximum cluster number of the order of 150-500. The measured heat of evaporation⁸ of a H_2O molecule from a $\text{H}^+(\text{H}_2\text{O})_n$ cluster with $n > 10$ is close to the bulk heat of evaporation of a H_2O molecule in water in the liquid phase ($\Delta H_v = 44.016$ kJ/mol), indicating that for large n , the water molecules in the cluster are in the liquid phase.

In the water medium, the addition of a small amount of ionic compound X^+Y^- will lead to ions dispersed over the water medium. When the medium is diluted enough with a X^+Y^- molar concentrations of 10^{-6} or lower, the ions can be considered to be well separated and isolated, and physical considerations similar to those for isolated ions are applicable. The strong polarizing power of the ions leads to a similar formation of $\text{X}^+(\text{H}_2\text{O})_n$ and $\text{Y}^-(\text{H}_2\text{O})_n$.

We consider the isothermal case and place an isolated ion of charge $q|e|$ at the origin $\mathbf{r}_0 = 0$. To study the response of the water medium to the presence of the charged ion, we can specify the properties of the water medium by the "equation of state" function $W(n, d)$ which is the energy per H_2O molecule. The function $W(n, d)$ depends on the temperature, the (number) density n , and the specific dipole moment d (the local average dipole moment per molecule). This function W arises, at least in principle, from all interactions between H_2O molecules. Because of the tetrahedron structure of the H_2O molecule,

there is the additional orientation dependence of the equation of state on the magnitude of the average dipole moment per molecule d . The dipole moment $\mathbf{d}(r)$ at \mathbf{r} , in general, has both a magnitude $d(\mathbf{r})$ and a direction.

The total energy of the medium is

$$E = \int W(n(\mathbf{r}), d(\mathbf{r})) n(\mathbf{r}) d\mathbf{r} - \int n(\mathbf{r}) \frac{qe^2 d(\mathbf{r}) \cos \theta(\mathbf{r})}{r^2} d\mathbf{r}. \quad (2)$$

Note that in the above equation, the interactions between H_2O molecules have been included in the equation of state $W(n, d)$.

The energy of the system (Eq.(2)) is a minimum when the angle θ is aligned along the electric lines of force of the ion, i.e. $\theta = 0$ for $q > 0$ and $\theta = \pi$ for $q < 0$. We shall assume that the dipole moments of the H_2O molecules have settled down such that this alignment has been achieved. Equilibrium is reached when the energy is stationary upon arbitrary variation of n and d ,

$$\delta E = \int \left[\frac{\delta}{\delta n} \left\{ W(n, d) n - n \frac{|q|e^2 d(r)}{r^2} \right\} \delta n + \frac{\delta}{\delta d} \left\{ W(n, d) n - n \frac{|q|e^2 d(\mathbf{r})}{r^2} \right\} \delta d \right] d\mathbf{r} = 0.$$

Thus, equilibrium of the medium occurs when

$$\frac{\delta}{\delta n} \left\{ W(n, d) n - n \frac{|q|e^2 d(r)}{r^2} \right\} = \left\{ \frac{\partial [W(n, d) n]}{\partial n} - \frac{|q|e^2 d(r)}{r^2} \right\} = 0 \quad (3)$$

and

$$\frac{\delta}{\delta d} \left\{ W(n, d) - \frac{|q|e^2 d(r)}{r^2} \right\} = 0. \quad (4)$$

Condition (3) implies that equilibrium is reached at those densities for which

$$W_{ext}(n, d) n = \{W(n, d) n - n |q|e^2 d(r)/r^2\} \quad (5)$$

is a minimum with respect to a variation in n , and (4) implies that equilibrium occurs for those dipole moment values where the energy per molecule

$$W_{ext}(n, d) = \{W(n, d) - |q|e^2 d(r)/r^2\} \quad (6)$$

is a minimum with respect to a variation in d . The second term in the above two equations represents the polarization force which moves the location of the energy minima to different densities or dipole moments.

4 Density and Dipole Moment Profile of H₂O Cluster for a Single State

It is instructive to give the structure of the H₂O cluster when the state of the water medium consists of a single state whose equation of state is described by

$$W(n, d) = \frac{1}{2}K_n \frac{(n - n_0)^2}{n} + \frac{1}{2}K_d(d - d_0)^2, \quad (7)$$

where n_0 is the equilibrium density, d_0 is the equilibrium specific dipole moment, K_n is stiffness parameter with respect to the density variation and is related to the compressibility of water, and K_d is the stiffness parameter with respect to the dipole moment variation. We assume again the alignment of the dipole moments around the ion, and we look for solutions of the density and the dipole moment around the equilibrium values. Then, Eq. (3) gives the density profile of the cluster as

$$n(r) = n_0 + \frac{\sqrt{|q|e^2 d(r)/K_n}}{r}. \quad (8)$$

Thus, the deviation of the cluster density from the equilibrium density is inversely proportional to the radial distance from the ion, depending on the compressibility K_n of water. Equation (4) leads to the dipole moment profile of the cluster as

$$d(r) = d_0 + \frac{|q|e^2}{K_d r^2}. \quad (9)$$

The deviation of the cluster dipole moment from equilibrium is inversely proportional to the square of the radial distance from the ion, depending on the stiffness of the variation of W with respect to d .

From this analysis, one notes that the density and the magnitude of the dipole moment of the H₂O cluster are greater than the corresponding quantities in the surrounding medium. It will be of interest to see whether such a difference may lead to observable sinking of the clusters due to gravity.

It is of interest to note the differences of two stiffness parameters K_n and K_d . The stiffness parameter K_n involves the compression of the medium. To compress water in the liquid phase, considerable energy is needed to overcome the repulsive overlap of the electronic densities of the molecules. One expects that the water medium is quite stiff against a change in density. On the other hand, the change of the specific dipole moment arises from the change of the local average of the vector sum of the dipole moments of the H₂O molecules, which can be brought about by reorienting the H₂O molecules without moving

their centers-of-mass. As the energy involved in making a rotational motion is considerably smaller than the energy required to bring two molecules closer than the equilibrium separation, one expects that the water medium is much softer against dipole moment distortions as compared to density distortions. That is, it is easier to change the specific dipole moment than the density.

5 Polymorphic States of H₂O in the Liquid Phase

The dipole moments for normal water are randomly oriented, and the (average) specific dipole moment is essentially zero. Other arrangements of the H₂O molecules different from that of the normal state of water are possible, and they may lead to polymorphic states of H₂O with different configurations, densities and dipole moments. Polymorphic states of H₂O in the solid phase manifest themselves in different structures of ice crystals where the tetrahedron structure of the molecule is maintained by joining the oxygen nuclei in tetrahedron network patterns, with a hydrogen nucleus between each link of two oxygen nuclei. These polymorphic states are well known¹⁷. We are naturally more interested in polymorphic states of H₂O in the liquid phase.

Polymorphic states of H₂O in the liquid phase are found experimentally in supercooled water by Mishima *et al.*^{18,19} and shown theoretically by Poole *et al.*^{21,22}, and by Roberts *et al.*²³. The polymorphic states of supercooled water exist as the low-density amorph (LDA) and the high-density amorph (HDA). The transition between the two polymorphic states has been observed to occur reversibly and abruptly at about 135° K and about 0.2 GPa with a volume change of 0.02 cm³/g and some hysteresis¹⁹. The LDA has a volume-pressure relation very similar to Ice Ih, while the HDA is similar to Ice V and VI at supercooled temperatures (see Fig. 1 of Ref. [19]). One can interpret LDA and HDA as configurations of excited energy minima in the liquid phase in which the normal ground states at that temperature are different configurations of ice in the solid phase. For a given temperature in which LDA (or HDA) is the lower energy ground state, the transition from the other excited HDA state (or LDA) will involve the release of heat, and such a release of heat has been observed experimentally¹⁹.

It is worth noting that metastable states in different energy minima have been found in many systems in physics. Hill and Wheeler discussed unstable shape isomers which differ from the stable ground state by their quadrupole moment²⁶. In this case, the quadrupole moment plays the role analogous to the order parameter in thermodynamic systems. Isomers with different quadrupole moments have been found experimentally in many nuclei and can be understood as the manifestation of multiple minima in the energy surface

as a function of the quadrupole moment²⁷. They are locally stable because they reside in the energy minima associated with their own local variations.

Recent theoretical work on supercooled water indicates that there are polymorphic states of water in which the local density can be an order parameter^{21,22,23}. The molecular dynamics computer simulations of Sciortino *et al.*²² show a first-order liquid-liquid phase transition for water molecules interacting among themselves with the ST2 model interaction. These two phases can co-exist at different spatial locations at a range of temperatures. They differ by about 15% in density and have different local structures, local dynamics, and mobility, with the molecules in the high-density phase much more mobile than the molecules in the low-density phase. In separate investigations on a supercooled, dense, equilibrium Lennard-Jones liquid using molecular dynamics, it is found that the more mobile particles form large-scale quasi-stable string-like clusters and their dynamics is correlated in a string-like motion^{24,25}. The fraction of these large clusters is about 5% of the liquid in the model considered.

Recently Roberts *et al.* found from theory and simulations of network-forming liquid that the polymorphic states occur quite generally in systems in which the molecules interact via strong directional intermolecular forces, as in the case of the tetrahedron H_2O molecules or Si atoms²³. The qualitative characteristics of the phase transition depend on the details of bonding and on the choice of the model parameters. For example, a calculated temperature-density phase diagram of a model network can exhibit a liquid-liquid phase transition in a pure substance, in addition to a vapor-liquid phase transition.

It will be of interest to study many tetrahedron networks similar to those of the ice crystals to see whether they lead to polymorphic states in the liquid phase. Furthermore, in view of the elongated shape of the clusters as observed in I_E water samples^{1,3}, it will be useful to study a network in which the simplest unit consists of two H_2O molecules with the H vertices of these molecules

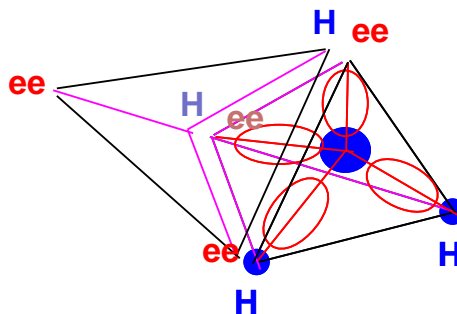


Fig. 2

in the vicinity of the ee vertices of the other molecule. The dipole moment of the whole complex is aligned along the symmetry axis of the two molecules, as in Figure 2. The repeated and parallel arrangement of these basic units along the same direction may lead to a state with a preferred direction as the symmetry direction, and may exhibit an elongated string-like behavior.

6 Structure of H₂O Cluster for Polymorphic States

We note in the last section the experimental observations of the existence of the polymorphic states in supercooled water^{18,19}. Theoretical supports for the occurrence of these polymorphic states in water comes from the directional nature of the interaction of tetrahedron molecules^{21,22,23}. There is also the occurrence of large-scale quasi-stable, string-like clusters in a simple Lennard-Jones liquid^{24,25}. It is therefore useful to explore the possibility of polymorphism for water at room temperature. The strong polarizing power of the ion makes it a useful tool for such an investigation.

Accordingly, we consider the possibility of polymorphic states of water at room temperature by representing the equation of state of water with an energy surface containing low-lying secondary minima where the normal ground state has order parameter d_0 , and metastable states with order parameter d_1 and d_2, \dots . The secondary minima are the anomalous states differing from the normal ground state water configuration by their order parameters which can be either the density or the specific dipole moment. Each energy minimum represents a configuration with distinct characteristics of the medium. The case for the dipole degree of freedom is shown schematically as the solid curve in Figure 3.

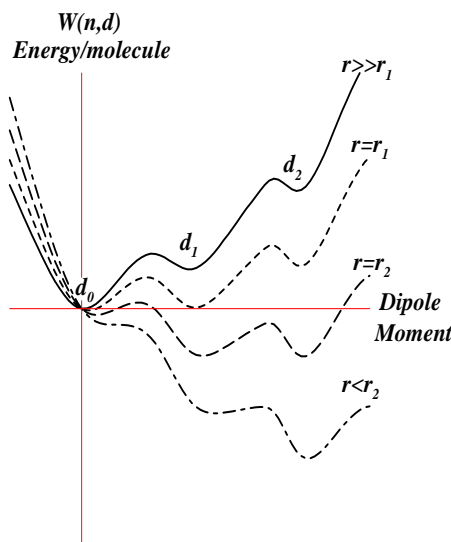


Fig.3. Energy per molecule as a function of the dipole moment for different distances r from the ion.

If the rate of change of the order parameter is rapid, the water molecule system will jump from the lowest energy surface to the higher energy surface, retaining the characteristics of its initial configuration, as in the case of large Landau-Zener jump probabilities²⁸. On the other hand, if the rate of change of the order parameter is small, then the intrinsic energy surface of the water molecule will follow the lowest surface represented by the solid curve in Figure 3, and the configuration of the system may change slowly from one minimum to the next as the dynamics evolves. In the polarization stage of the pro-

cess, we shall consider only this case of slow change of the order parameters. The anomalous states represented by the secondary minima at d_1 and d_2 are separated from the minimum for the normal state at d_0 by a barrier.

Assuming again the alignment of the molecular dipole moments along the lines of force of the ion, one can use the equilibrium conditions (3) and (4) to study the profile of dipole moment and density around the cluster. Consider first the dipole moment as the order parameter with an equation of state $W(n, d)$ in the form of the solid curve shown in Figure 3. The equilibrium dipole moment is determined by the condition that the function $W_{\text{ext}}(n, d)$ is a minimum of d . As $W_{\text{ext}}(n, d) = W(n, d) - |q|e^2d/r^2$, the minimum will be located at different values of d for various values of r . In Fig. 3 the solid curve gives $W_{\text{ext}}(n, d)$ at a distance far from the ion in the bulk part of the water medium. The metastable minima d_1 and d_2 are above the normal ground state d_0 . At a distance r_1 from the ion, the polarization term ($-|q|e^2d/r^2$) proportional to d distorts the function W_{ext} such that the minimum around d_1 is on the same level as that around d_0 , and a state of coexistence of the two states is possible. At a shorter distance, the dipole moment will make a transition to d_2 . Similarly, at distances closer than r_2 , the minima at d_2 is pulled down lower than the minimum around d_1 , and the system will make a transition to the dipole moment around d_2 . Thus, the dipole moment is $\sim d_0$ for $r > r_1$, is $\sim d_1$ for $r_1 > r > r_2$ and is $\sim d_2$ for $r_2 > r$, and so on. Thus, in the presence of polymorphic states of water, the local dipole moment of the cluster abruptly changes as a function of the radial separation from the ion, corresponding to the different minima brought down by the polarizing interaction.

One can use a similar argument to discuss the density profile of the medium around an ion. The equilibrium density is determined by the condition that the function $nW_{\text{ext}}(n, d) = nW(n, d) - n|q|e^2d/r^2$ is a minimum with respect to a variation in n . If the function $W_{\text{ext}}(n, d)$ possesses secondary minima, then $nW_{\text{ext}}(n, d)$ will also possess multiple minima. Using arguments similar to those for the dipole moments, one finds that in the presence of polymorphic states in density, the local density around a cluster changes abruptly as a function of the radial distance from the ion. After equilibrium is reached, water molecules at different distances will have different densities, being greater at shorter distances from the ion.

The abrupt changes of density or dipole moment arise only when the heights of the secondary minima in these two degrees of freedom are not too large so that they can be pulled down by the polarizing power of the ion. If the heights of these secondary minima are very large, then, for all intents and purposes, the medium is essentially a single state where the secondary minima

play no role.

7 Cluster Interaction and Fragmentation

After equilibrium is reached and the clusters formed around the ions, each cluster remains charged, and there is a Coulombic interaction between different clusters. Each cluster has a radius of about 10 \AA , and the Coulomb interaction energy between two touching clusters of opposite charge is about 0.7 eV which is still considerable. It may provide sufficient attractive interaction for the clusters to arrange themselves in an orderly manner, forming clusters of greater sizes (superclusters) with many $X^+(H_2O)_n$ and $Y^-(H_2O)_n$ entities. Another interesting possibility is the formation of a bridge linking the two clusters of opposite charge between which the dipole moments of the H_2O molecules line up in the same direction. It is of interest to examine in I_E water whether superclusters or bridges of H_2O molecules are components of the anomalous states in I_E water. Thus, the study of these clusters in I_E water will provide information on the stability and the interactions of the $X^+(H_2O)_n$ and $Y^-(H_2O)_n$ in aqueous solutions.

If the liquid is shaken vigorously after equilibrium is reached, then the cluster will fragment into many small domains. In each domain, the dipole moment has been properly aligned by the ion. If the water medium has only a single phase, these domains will relax and will return to the state of the normal water, with the orientation of the dipole moments of the H_2O molecules becoming randomized again. No new anomalous state will be formed as a stable entity.

The situation will be different if there are polymorphic states of water and the domains which break away from the cluster contain metastable polymorphic states, which have been produced under the strong field of the polarizing ion. Being a polymorphic state stable under local variations of its order parameters, these domains will not relax to the normal state of water. They will remain metastable and may coalesce with other similar domains. Fragmented domains of H_2O can also act as seeds for the growth of greater regions of polymorphic states. In this case, anomalous polymorphic states will contain metastable domains of H_2O molecules for which the dipole moment or the density may be different from that in the normal state.

8 Conclusions and Discussions

The anomalous states of water are peculiar and unexpected. Their existence may be connected to the occurrence of metastable polymorphic states of water at room temperature. It is therefore important to confirm or to refute the

observations of these anomalous states by independent experimental investigations.

Looking at the process of the formation of the anomalous states, one finds that isolated ions have great polarizing power which attracts water molecules around it. Stable clusters in free assembly have been copiously found experimentally and their existence in dilute aqueous solutions is expected. The large polarizing power of the ionic charge leads to great change of the dipole moment and density of the medium around the ion. These changes depend on the stiffness of the equation of state against the variation of density and dipole moments. If there are low-lying polymorphic states of the liquid, the polarizing action of the ion will lead to local densities and local dipole moments which change abruptly as a function of the separation from the ion, being greater at shorter distances from the ion.

Fragmentation of the clusters upon vigorous shaking will produce domains of the liquid where the dipole moments are aligned. The coalescence of these domains and the seeding of these regions may allow the formation of polymorphic states of the liquid if these polymorphic states are possible metastable configurations of the liquid. Pending further experimental confirmations, the anomalous states of the I_E water may be such a substance.

The presence of the polymorphic state can be examined by looking for the decay of the metastable I_E state. It can also be studied by exciting the I_E state above the barrier which will lead to a change of the I_E state to the normal state, and will deplete the I_E water population. One can also measure the dielectric properties of the I_E water to show an enhanced dipole moment of the I_E water. The difference in the dielectric constants as discussed by Lo *et al.*² needs to be analyzed theoretically to understand its implications on the nature of the dipole moments in the anomalous states.

The foregoing discussions in the last few sections can be carried over to discuss many other liquids in which the molecules in the liquid have permanent dipole moments. Because the polarizing interaction for an aligned dipole depends on $-|q|e^2d/r^2$, the interaction is greater, the greater the static electric dipole moment of a single molecule. Therefore, the addition of a small amount of ionic compound on a liquid whose molecules have a large static dipole moment will lead to a very strong clustering of the molecules around the ion. They can be well utilized to study polymorphism in these liquids to see whether domains of anomalous states with properties different from those in the ground states may exist in these liquids.

Acknowledgments

The authors would like to thank Profs. A. A. Chialvo and S. Christian for helpful discussions. The research of CYW is sponsored by the USDOE under Contract DE-AC05-96OR22464 managed by Lockheed Martin Energy Research Corp.

References

1. S.-Y. Lo, *Modern Phys. Lett.* **19**, 909 (1996).
2. S.-Y. Lo *et al.*, *Modern Phys. Lett.* **19**, 921 (1996).
3. S.-Y. Lo, Proceedings of this Symposium, 1997.
4. A. Good, D. A. Durden, and P. Kebarle, *J. Chem. Phys.* **52**, 212 (1970).
5. R. Yamdagni and P. Kebarle, *Can. J. Chem.* **52**, 2249 (1974).
6. G. Caldwell and P. Kebarle, *Can. J. Chem.* **63**, 1399 (1970).
7. T. Schindler, C. Berg, G. Niedner-Schatteburg, and V. E. Bondybey, *Chem. Phys.* **201**, 491 (1995).
8. T. Schindler, C. Berg, G. Niedner-Schatteburg, and V. E. Bondybey, *Chem. Phys. Lett.* **229**, 57 (1995).
9. A. A. Viggiano *et al.*, *J. Phys. Chem.* **94**, 8194 (1990).
10. X. Yang, X. Zhang, and A. W. Castleman, Jr. *J. Phys. Chem.* **95**, 8520 (1991).
11. K. Hiraoka, S. Mizuse, and S. Yamabe, *J. Phys. Chem.* **92**, 3943 (1988).
12. J. W. Larson and T. B. McMahon, *J. Am. Chem. Soc.* **106**, 517 (1984).
13. J. Coe, *Chem. Phys. Lett.* **229**, 161 (1994).
14. E. E. Tucker and S. D. Christian, *J. Am. Chem. Soc.* **106**, 517 (1984).
15. L. X. Deng, J. E. Rice, J. Caldwell, and P. Kollman, *J. Am. Chem. Soc.* **113**, 2481 (1991).
16. A. A. Chialvo, P. T. Cummings, J. M. Simonson, and R. E. Mesmer, Proceedings of the Fifth International Conference on Hydrothermal Reactions, Gatlinburg, June 1997, (Edited by D. A. Palmaer *et al.*), pp. 157-160.
17. N. Fletcher, *The Chemical Physics of Ice*, Cambridge University Press, 1970.
18. O. Mishima, L. D. Calvert, and E. Whalley, *Nature* **310**, 393 (1984).
19. O. Mishima, *Jour. Chem. Phys.* **100**, 5910 (1994).
20. R. Holyst, *Encyclopedia of Applied Physics*, (<http://xxx.lanl.gov/abs/cond-mat/?9603062>).
21. P. H. Poole, T. Grande, C. A. Angell, and P. F. McMillan, *Science* **275**, 322 (1997).
22. F. Sciortino, P. H. Poole, U. Essmann, and H.E. Stanley, *Phys. Rev. E*.

- 55**, 727 (1997).
23. C. J. Roberts, G. Karayiannakis, and P. G. Debenedetti, AICHE Talk, (November, 1997).
 24. W. Kob, C. Donati, S. J. Plimpton, P. H. Poole, and S. C. Glotzer, *Phys. Rev. Lett.* **79**, 2827 (1997).
 25. C. Donati, J. K. Douglas, W. Kob, S. J. Plimpton, P. H. Poole, and S. C. Glotzer, (<http://xxx.lanl.gov/abs/cond-mat/?9706277>).
 26. D. L. Hill and J. A. Wheeler, *Phys. Rev.* **89**, 1102 (1953).
 27. M. Brack, J. Damgaard, A. S. Jensen, H. C. Pauli, V. M. Strutinsky, and C. Y. Wong, *Rev. Mod. Phys.* **44**, 320 (1972).
 28. L. D. Landau, *Z. Phys. Sow. Un.* **2**, 46 (1932); C. Zener, *Proc. Roy. Soc. (London)* **A137**, 696 (1932).